

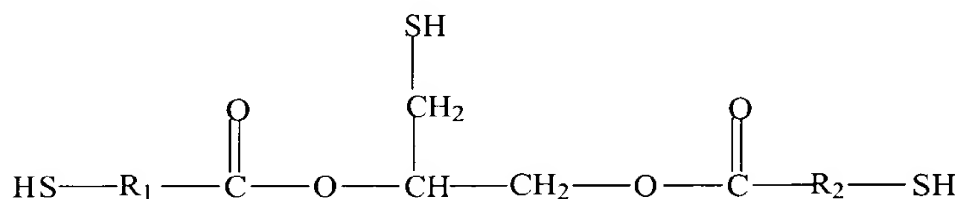
We claim:

1. A method of preparing a polymerizate comprising the step of polymerizing a two-component composition comprised of:

- 5 (a) a first component containing at least one polycyanate reactant having at least two functional groups selected from isocyanate, isothiocyanate and combinations thereof, the polycyanate reactant being the reaction product of,
- (i) a polythiol monomer having at least two thiol groups; and
- (ii) a polycyanate monomer having at least two functional
- 10 groups selected from isocyanate, isothiocyanate and combinations thereof; and
- (b) a second component containing at least one polyamine reactant having at least two functional groups selected from primary amine, secondary amine and combinations thereof.
- 15 2. The method of claim 1 wherein said first component further comprises (iii) a reactive hydrogen material having at least two reactive hydrogen groups, the reactive hydrogen material being selected from the group consisting of polyols and materials having both hydroxyl and thiol groups; and mixtures thereof.
- 20 3. The method of claim 1 wherein the relative amounts of (i) and (ii) in said first component are selected such that the molar equivalents ratio of $(\text{NCO} + \text{NCS})/(\text{SH})$ is greater than 1.0.
4. The method of claim 2 wherein the relative amounts of (i), (ii) and (iii) being in said first component are selected such that the molar equivalents ratio of $(\text{NCO} + \text{NCS})/(\text{SH} + \text{OH})$ is greater than 1.0.
- 25 5. The method of claim 1 wherein said first component and said second component are selected such that when they are polymerized, the resulting
- 30 polymerizate has a refractive index of at least 1.6, an Abbe number of at least 33 and an initial Barcol hardness of at least 1.

6. The method of claim 2 wherein the relative amounts of (i), (ii) and (iii) are selected such that the molar equivalents ratio of (NCO + NCS)/(SH + OH) is from 1.2:1.0 to 4.0:1.0.

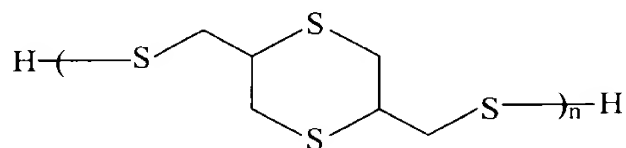
- 5 7. The method of claim 1 wherein said polythiol monomer is selected from the group consisting of 2,5-dimercaptomethyl-1,4-dithiane, 2,2'-thiodiethanethiol, pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptopropionate), trimethylolpropane tris(3-mercaptopropionate), trimethylolpropane tris(2-mercaptopropionate), 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol, 4-tert-butyl-1,2-benzenedithiol, 4,4'-thiodibenzenethiol, benzenedithiol, ethylene glycol di(2-mercaptopropionate), ethylene glycol di(3-mercaptopropionate), poly(ethylene glycol) di(2-mercaptopropionate) and poly(ethylene glycol) di(3-mercaptopropionate), a polythiol represented by the general formula:



- 15 wherein R_1 and R_2 are each independently selected from straight or branched chain alkylene, cyclic alkylene, phenylene and C_1 - C_9 alkyl substituted phenylene, and oligomers of said polythiols; and mixtures of said polythiol monomers.

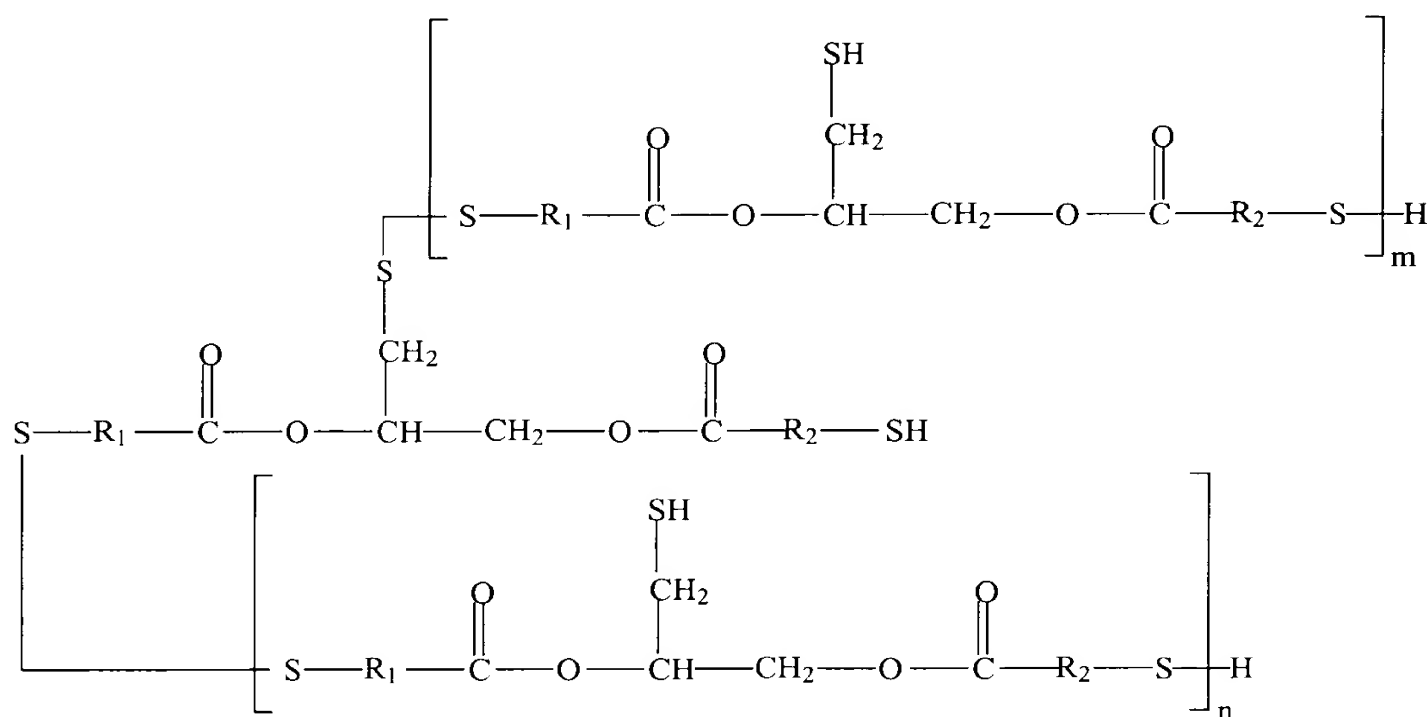
- 20 8. The method of claim 7, wherein said polythiol oligomer has disulfide linkages and is prepared by reacting a polythiol monomer, with sulfur, in the presence of a basic catalyst.

9. The method of claim 7 wherein said polythiol oligomer is represented by the general formula:



wherein n is an integer from 1 to 21.

10. The method of claim 7 wherein said polythiol oligomer is represented by the general formula:

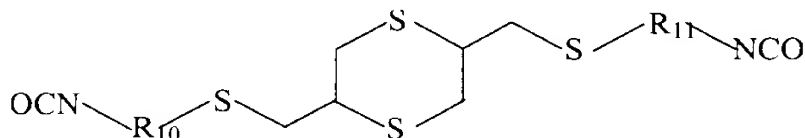


5 wherein R₁ and R₂ are each independently selected from straight or branched chain alkylene, cyclic alkylene, phenylene and C₁-C₉ alkyl substituted phenylene and n and m are independently integers from 0 to 21 such that n + m is at least 1.

11. The method of claim 1 wherein said polycyanate monomer is a
10 polycyanate having at least two isocyanate groups.

12. The method of claim 1 wherein said polycyanate monomer is a polycyanate having one or more sulfur atoms in its backbone.

13. The method of claim 12 wherein the polycyanate monomer having one or more sulfur atoms in its backbone is one having the general structure:

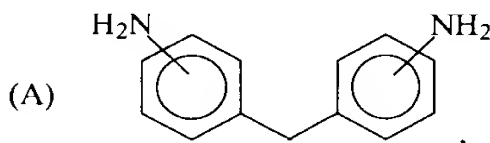


wherein R_{10} and R_{11} are each independently C_1 to C_3 alkyl.

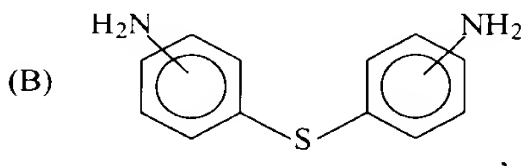
14. The method of claim 11 wherein said polycyanate monomer is selected from the group consisting of α, α' -xylene diisocyanate, $\alpha, \alpha, \alpha', \alpha'$ -tetramethylxylene diisocyanate, isophorone diisocyanate, bis(isocyanatocyclohexyl)methane, ortho-toluidine diisocyanate, ortho-tolylidine diisocyanate, ortho-tolylene diisocyanate and 4,4'-diphenylmethane diisocyanate, and mixtures of said polycyanate monomers.

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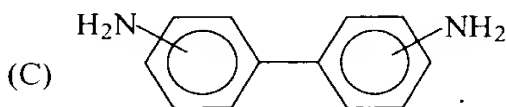
15. The method of claim 1 wherein said polyamine reactant of said second component is selected from the group consisting of ethyleneamines, C_1 - C_3 dialkyl toluenediamine, methylene dianiline, trimethyleneglycol di(para-aminobenzoate), a diamine represented by the general formula (A):



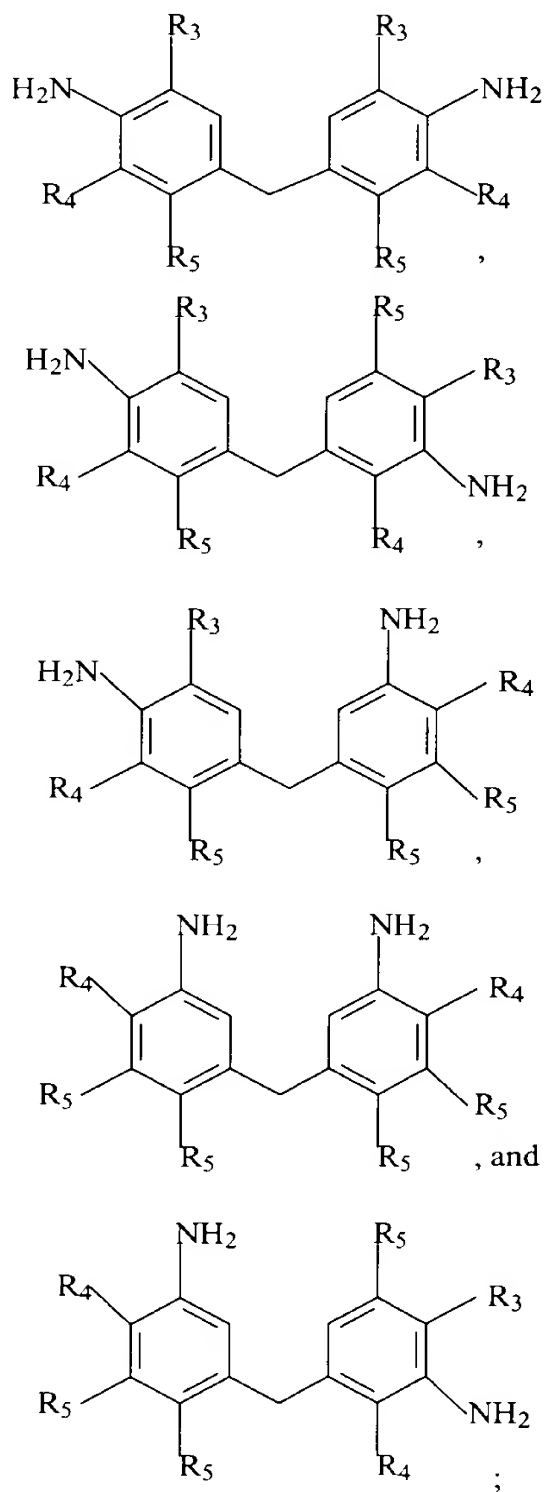
15 a diamine represented by the general formula (B):



and a diamine represented by the general formula (C):

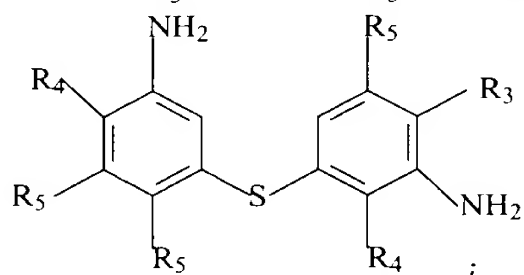
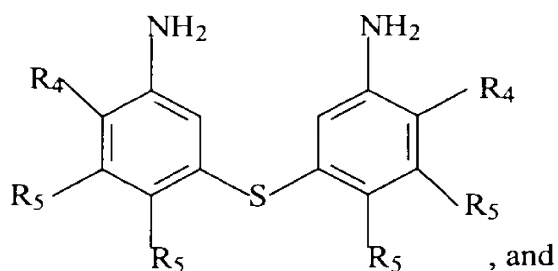
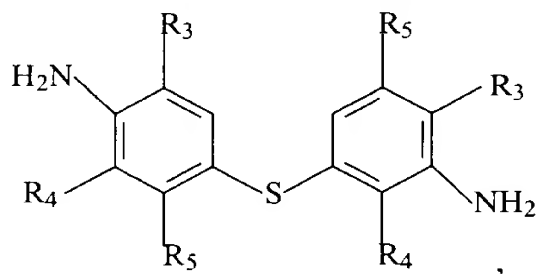
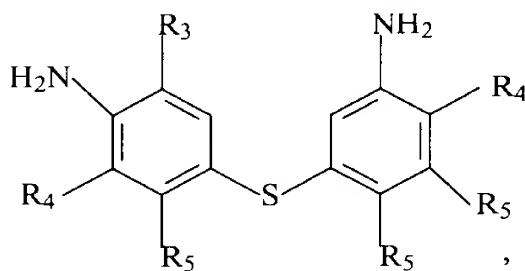
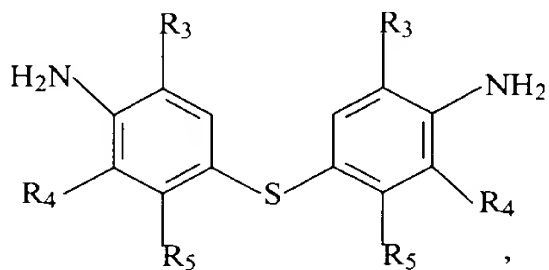


16. The method of claim 15 wherein the diamine of general formula (A) is selected from one or more of the group consisting of:



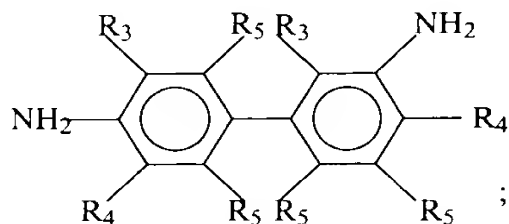
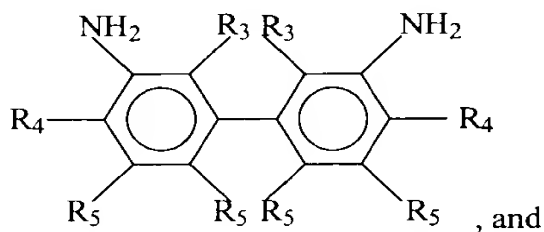
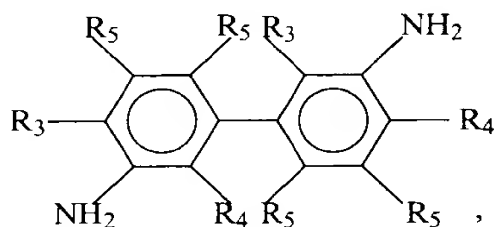
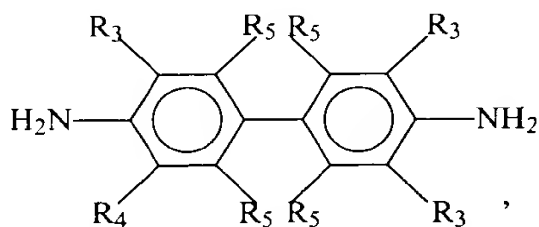
wherein R_3 and R_4 are each independently C_1 - C_3 alkyl, and R_5 is selected from hydrogen and halogen, and mixtures of said diamines.

17. The method of claim 15 wherein the diamine of general formula (B) is
5 selected from one or more of the group consisting of:



wherein R_3 and R_4 are each independently C_1 - C_3 alkyl, and R_5 is selected from hydrogen and halogen, and mixtures of said diamines.

- 5 18. The method of claim 15 wherein the diamine of general formula (C) is selected from one or more of the group consisting of:



- 10 wherein R_3 and R_4 are each independently C_1 - C_3 alkyl, and R_5 is selected from hydrogen and halogen, and mixtures of said diamines.

19. The method of claim 1 further comprising the step of adding a catalyst to said two-component composition.

5 20. The method of claim 16 wherein said catalyst is selected from the group consisting of tertiary amines and organometallic compounds.

21. The method of claim 1 further comprising the step of :
mixing said first component and said second component.

10

22. The method of claim 1 further comprising the step of :
degassing said first component.

15

23. The method of claim 1 further comprising the step of :
degassing said second component.

24. The method of claim 21 further comprising the step of :
adding the mixture to a mold.

20

25. The method of claim 24 further comprising the step of :
heating the mold and the mixture of said first component and said second
component within it.

26. The method of claim 25 wherein said heating step further includes heating
25 the mold and said mixture to a temperature of up to 200°C over a period of from 0.5
to 72 hours.

27. The method of claim 1 wherein said first component and said second
component are polymerized together in amounts sufficient to provide a molar
30 equivalent ratio of (NCO + NCS) groups to (-NH₂ + -NH-) groups of from 0.5 to 3.0.

28. The method of claim 1 further comprising the step of adding additives selected from the group consisting of light stabilizers, heat stabilizers, antioxidants, ultraviolet light absorbers, mold release agents, static (non-photochromic) dyes, pigments and flexibilizing additives and anti-yellowing additives; and mixtures of said additives.

29. The method of claim 28 wherein the additives are present in said two component composition, in an amount up to 10% by weight of said two component composition.

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30. The method of claim 1 wherein said polymerizate further comprises a photochromic substance.

31. A polymerizate prepared by polymerizing a two-component composition comprised of:

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(a) a first component containing at least one polycyanate reactant having at least two functional groups selected from isocyanate, isothiocyanate and combinations thereof, the polycyanate reactant being the reaction product of,

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(i) a polythiol monomer having at least two thiol groups; and
(ii) a polycyanate monomer having at least two functional groups selected from isocyanate, isothiocyanate and combinations thereof; and

(b) a second component containing at least one polyamine reactant having at least two functional groups selected from primary amine, secondary amine and combinations thereof.

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32. The polymerizate of claim 31 wherein said first component further comprises (iii) a reactive hydrogen material having at least two reactive hydrogen groups, the reactive hydrogen material being selected from the group consisting of polyols and materials having both hydroxyl and thiol groups, and mixtures thereof.

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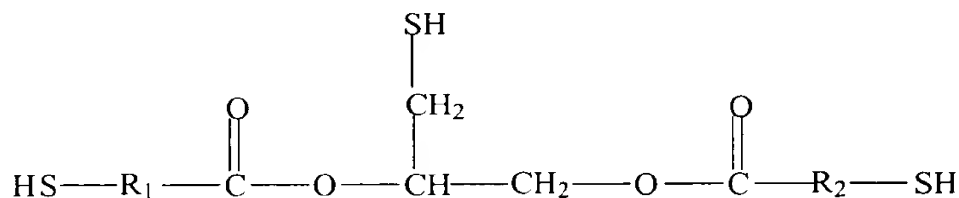
33. The polymerizate of claim 31 wherein the relative amounts of (i) and (ii) in said first component are selected such that the molar equivalents ratio of (NCO + NCS)/(SH) is greater than 1.0.

5 34. The polymerizate of claim 32 wherein the relative amounts of (i), (ii) and (iii) being in said first component are selected such that the molar equivalents ratio of (NCO + NCS)/(SH + OH) is greater than 1.0.

35. The polymerizate of claim 31 wherein said first component and said
10 second component are selected such that when they are polymerized, the resulting polymerizate has a refractive index of at least 1.6, an Abbe number of at least 33 and an initial Barcol hardness of at least 1.

36. The polymerizate of claim 34 wherein the relative amounts of (i), (ii) and
15 (iii) are selected such that the molar equivalents ratio of (NCO + NCS)/(SH + OH) is from 1.2:1.0 to 4.0:1.0.

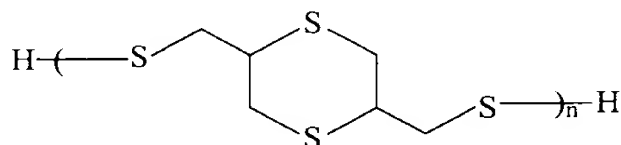
37. The polymerizate of claim 31 wherein said polythiol monomer is selected from the group consisting of 2,5-dimercaptomethyl-1,4-dithiane, 2,2'-
20 thiodiethanethiol, pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoacetate), trimethylolpropane tris(3-mercaptopropionate), trimethylolpropane tris(2-mercaptoacetate), 4-mercaptopomethyl-3,6-dithia-1,8-octanedithiol, 4-tert-butyl-1,2-benzenedithiol, 4,4'-thiodibenzenethiol, benzenedithiol, ethylene glycol di(2-mercaptoacetate), ethylene glycol di(3-mercaptopropionate),
25 poly(ethylene glycol) di(2-mercaptoacetate) and poly(ethylene glycol) di(3-mercaptopropionate) and a polythiol represented by the general formula:



wherein R_1 and R_2 are each independently selected from straight or branched chain alkylene, cyclic alkylene, phenylene and C_1 - C_9 alkyl substituted phenylene, and oligomers of said polythiols;, and mixtures of said polythiol monomers.

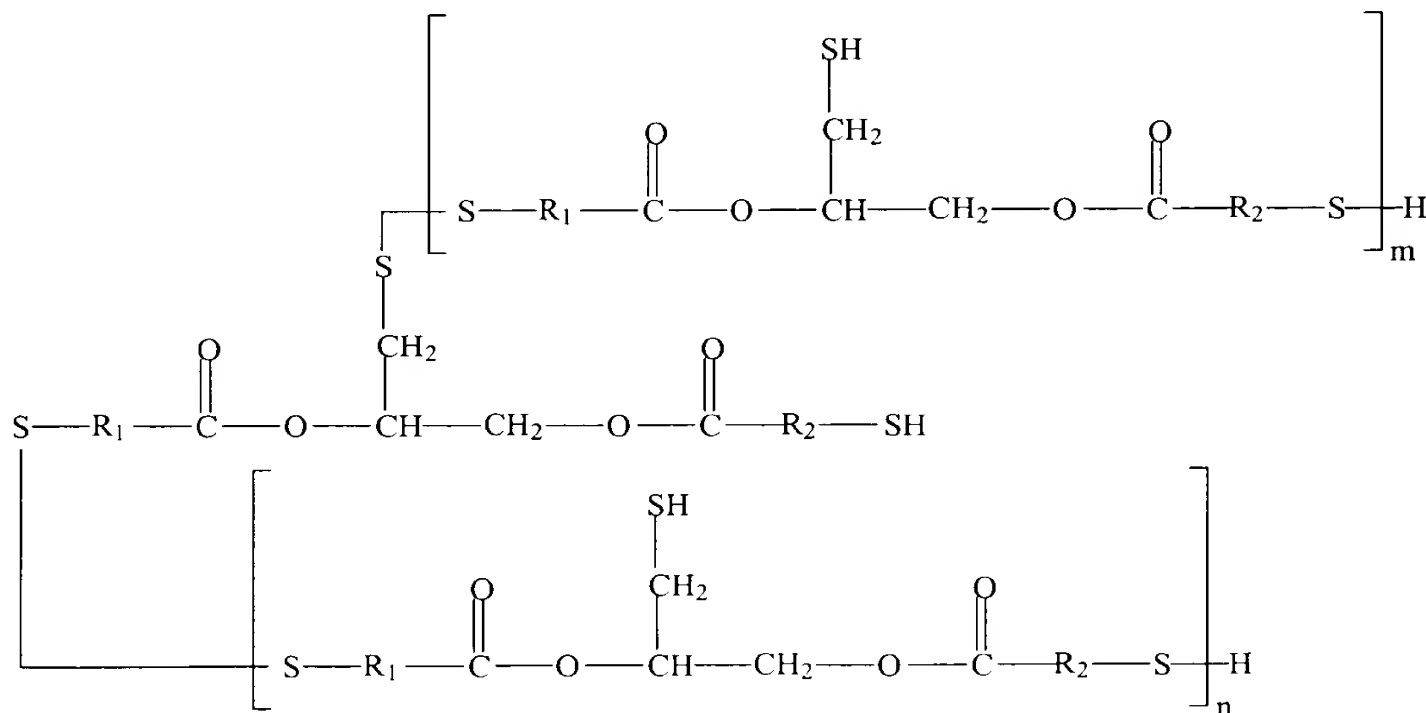
- 5 38. The polymerizate of claim 37 wherein said polythiol oligomer has disulfide linkages and is prepared by reacting a polythiol monomer with sulfur in the presence of a basic catalyst.

39. The polymerizate of claim 37 wherein said polythiol oligomer is
10 represented by the general formula:



wherein n is an integer from 1 to 21.

40. The polymerizate of claim 37 wherein said polythiol oligomer is represented by the general formula:

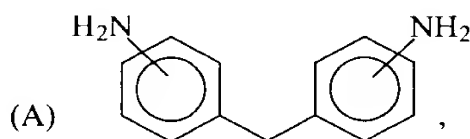


wherein R_1 and R_2 are each independently selected from straight or branched chain alkylene, cyclic alkylene, phenylene and C_1 - C_9 alkyl substituted phenylene and n and m are independently integers from 0 to 21 such that $n + m$ is at least 1.

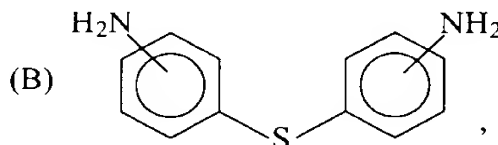
5 41. The polymerizate of claim 31 wherein said polycyanate monomer is a polycyanate having at least two isocyanate groups.

42. The polymerizate of claim 41 wherein said polycyanate monomer is selected from the group consisting of α, α' -xylene diisocyanate, $\alpha, \alpha, \alpha', \alpha'$ -
10 tetramethylxylene diisocyanate, isophorone diisocyanate, bis(isocyanatocyclohexyl)methane, ortho-toluidine diisocyanate, ortho-tolylidene diisocyanate, ortho-tolylene diisocyanate and 4,4'-diphenylmethane diisocyanate, , and mixtures of said polycyanate monomers.

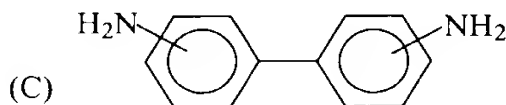
15 43. The polymerizate of claim 31 wherein said polyamine reactant of said second component is selected from the group consisting of ethyleneamines, C_1 - C_3 dialkyl toluenediamine, methylene dianiline, trimethyleneglycol di(para-aminobenzoate), a diamine represented by the general formula (A):



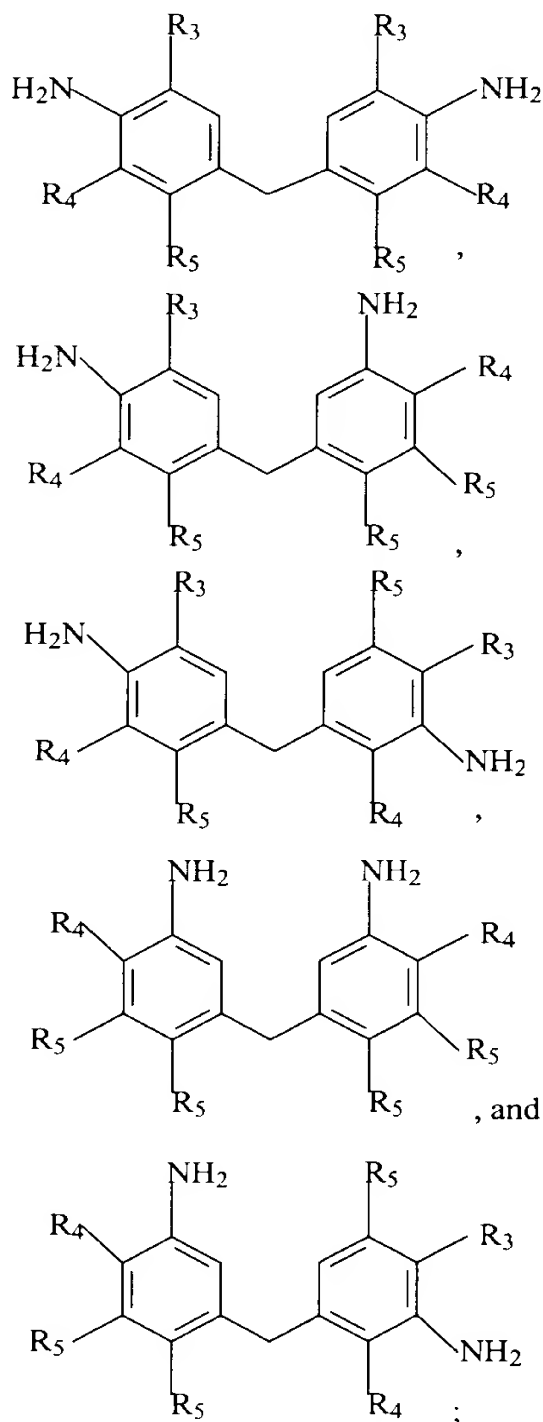
a diamine represented by the general formula (B):



20 and a diamine represented by the general formula (C):



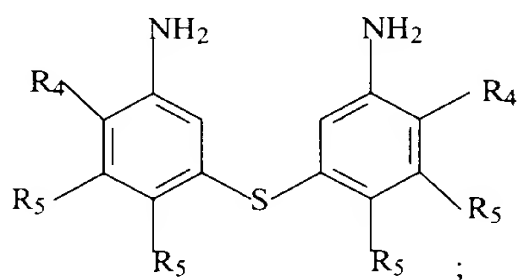
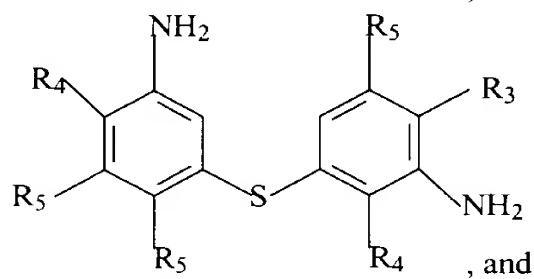
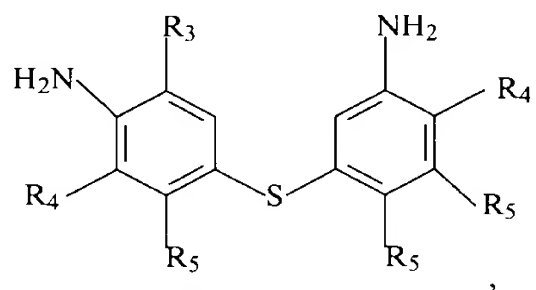
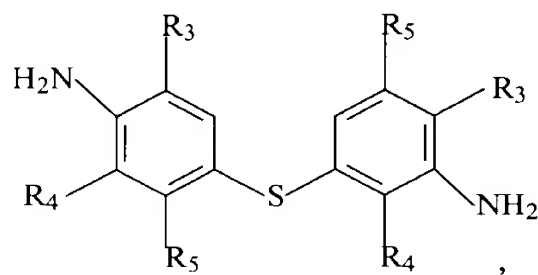
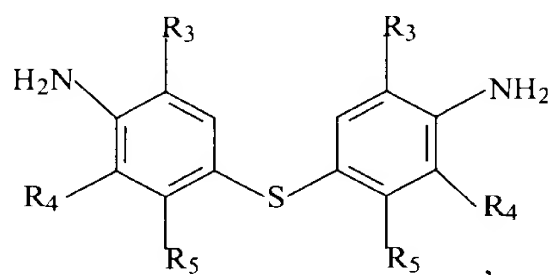
44. The polymerizate of claim 43 wherein the diamine of general formula (A) is selected from one or more of the group consisting of:



wherein R₃ and R₄ are each independently C₁-C₃ alkyl, and R₅ is selected from
5 hydrogen and halogen, and mixtures of said diamines.

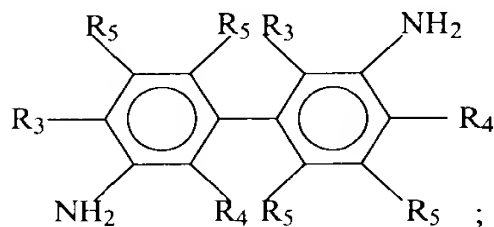
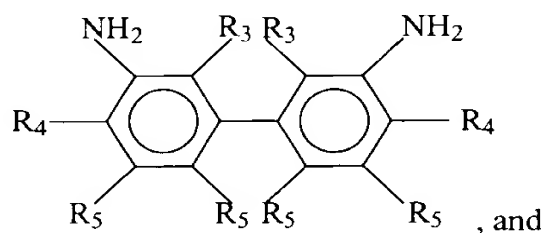
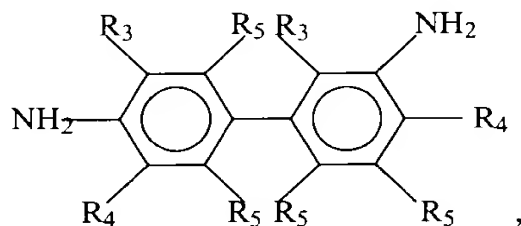
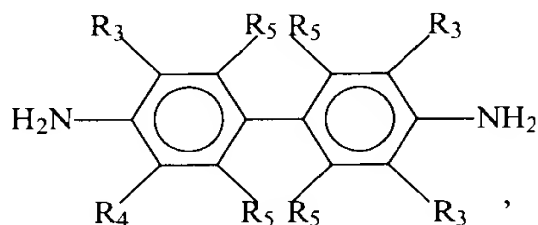
45. The polymerizate of claim 43 wherein the diamine of general formula (B) is selected from one or more of the group consisting of:

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wherein R_3 and R_4 are each independently C_1 - C_3 alkyl, and R_5 is selected from hydrogen and halogen, and mixtures of said diamines.

- 5 46. The polymerizate of claim 43 wherein the diamine of general formula (C) is selected from one or more of the group consisting of:



- 10 wherein R_3 and R_4 are each independently C_1 - C_3 alkyl, and R_5 is selected from hydrogen and halogen, and mixtures of said diamines.

47. The polymerizate of claim 31 wherein a catalyst is added to said two-component composition to promote the polymerization.

48. The polymerizate of claim 47 wherein said catalyst is selected from the group consisting of tertiary amines and organometallic compounds.

5 49. The polymerizate of claim 31 wherein the polymerization process further comprises the step of :

 mixing said first component and said second component.

 50. The polymerizate of claim 31 wherein the polymerization further
10 comprises the step of :

 degassing said first component.

 51. The polymerizate of claim 31 wherein the polymerization further
comprises the step of :

15 degassing said second component.

 52. The polymerizate of claim 49 wherein the polymerization further
comprising the step of:

 adding the mixture to a mold.

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 53. The polymerizate of claim 52 wherein the polymerization further
comprising the step of:

 heating the mold and the mixture of said first component and said second
component within it.

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 54. The polymerizate of claim 53 wherein said heating step further includes
heating the mold and said mixture to a temperature of up to 200°C over a period of
from 0.5 to 72 hours.

30 55. The polymerizate of claim 31 wherein said first component and said
second component are polymerized together in amounts sufficient to provide a molar
equivalent ratio of (NCO + NCS) groups to (-NH₂ + -NH-) groups of from 0.5 to 3.0.

56. The polymerizate of claim 31 further comprising additives selected from the group consisting of light stabilizers, heat stabilizers, antioxidants, ultraviolet light absorbers, mold release agents, static (non-photochromic) dyes, pigments and
5 flexibilizing additives and anti-yellowing additives; and mixtures of said additives.

57. The polymerizate of claim 56 wherein the additives are present in said polymerizate in an amount up to 10% by weight of said polymerizate.

10 58. The polymerizate of claim 31 further comprising a photochromic substance.

59. A photochromic article derived from a polymerizate prepared by polymerizing a two-component composition comprised of:

15 (a) a first component containing at least one polycyanate reactant having at least two functional groups selected from isocyanate, isothiocyanate and combinations thereof, the polycyanate reactant being the reaction product of,
(i) a polythiol monomer having at least two thiol groups; and
(ii) a polycyanate monomer having at least two functional
20 groups selected from isocyanate, isothiocyanate and combinations thereof; and
(b) a second component containing at least one polyamine reactant having at least two functional groups selected from primary amine, secondary amine and combinations thereof.

25 60. The photochromic article of claim 59 wherein said first component further comprises (iii) a reactive hydrogen material having at least two reactive hydrogen groups, the reactive hydrogen material being selected from the group consisting of polyols and materials having both hydroxyl and thiol groups, and mixtures thereof.

30 61. The photochromic article of claim 59 wherein the relative amounts of (i) and (ii) in said first component are selected such that the molar equivalents ratio of $(\text{NCO} + \text{NCS})/(\text{SH})$ is greater than 1.0.

62. The photochromic article of claim 60 wherein the relative amounts of (i), (ii) and (iii) being in said first component are selected such that the molar equivalents ratio of (NCO + NCS)/(SH + OH) is greater than 1.0.

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63. The photochromic article of claim 59 wherein said first component and said second component are selected such that when they are polymerized, the resulting polymerizate has a refractive index of at least 1.6, an Abbe number of at least 33 and an initial Barcol hardness of at least 1.

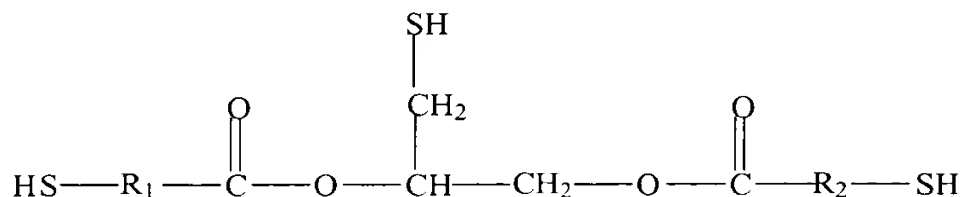
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64. The photochromic article of claim 60 wherein the relative amounts of (i), (ii) and (iii) are selected such that the molar equivalents ratio of (NCO + NCS)/(SH + OH) is from 1.2:1.0 to 4.0:1.0.

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65. The photochromic article of claim 59 wherein said polythiol monomer is selected from the group consisting of 2,5-dimercaptomethyl-1,4-dithiane, 2,2'-thiodiethanethiol, pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptopropionate), trimethylolpropane tris(3-mercaptopropionate), trimethylolpropane tris(2-mercaptopropionate), 4-mercaptopropionate-1,8-octanedithiol, 4-tert-butyl-1,2-benzenedithiol, 4,4'-thiodibenzenethiol, benzenedithiol, ethylene glycol di(2-mercaptopropionate), ethylene glycol di(3-mercaptopropionate), poly(ethylene glycol) di(2-mercaptopropionate) and poly(ethylene glycol) di(3-mercaptopropionate), a polythiol represented by the general formula:

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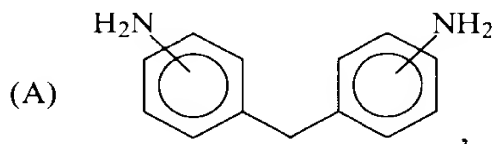
25 wherein R₁ and R₂ are each independently selected from straight or branched chain alkylene, cyclic alkylene, phenylene and C₁-C₆ alkyl substituted phenylene, and oligomers of said polythiols; and mixtures of said polythiol monomers.

69. The photochromic article of claim 59 wherein said polycyanate monomer is a polycyanate having at least two isocyanate groups.

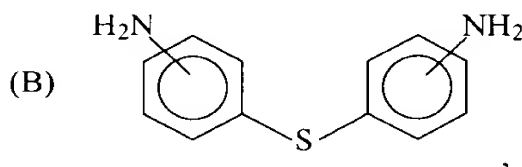
70. The photochromic article of claim 69 wherein said polycyanate monomer is selected from the group consisting of α,α' -xylene diisocyanate, $\alpha,\alpha,\alpha',\alpha'$ -tetramethylxylene diisocyanate, isophorone diisocyanate, bis(isocyanatocyclohexyl)methane, ortho-toluidine diisocyanate, ortho-tolyldine diisocyanate, ortho-tolylene diisocyanate and 4,4'-diphenylmethane diisocyanate, , and mixtures of said polycyanate monomers.

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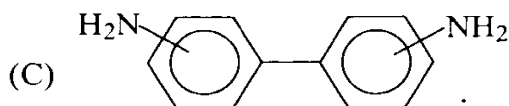
71. The photochromic article of claim 59 wherein said polyamine reactant of said second component is selected from the group consisting of ethyleneamines, C_1 - C_3 dialkyl toluenediamine, methylene dianiline, trimethyleneglycol di(para-aminobenzoate), a diamine represented by the general formula (A):



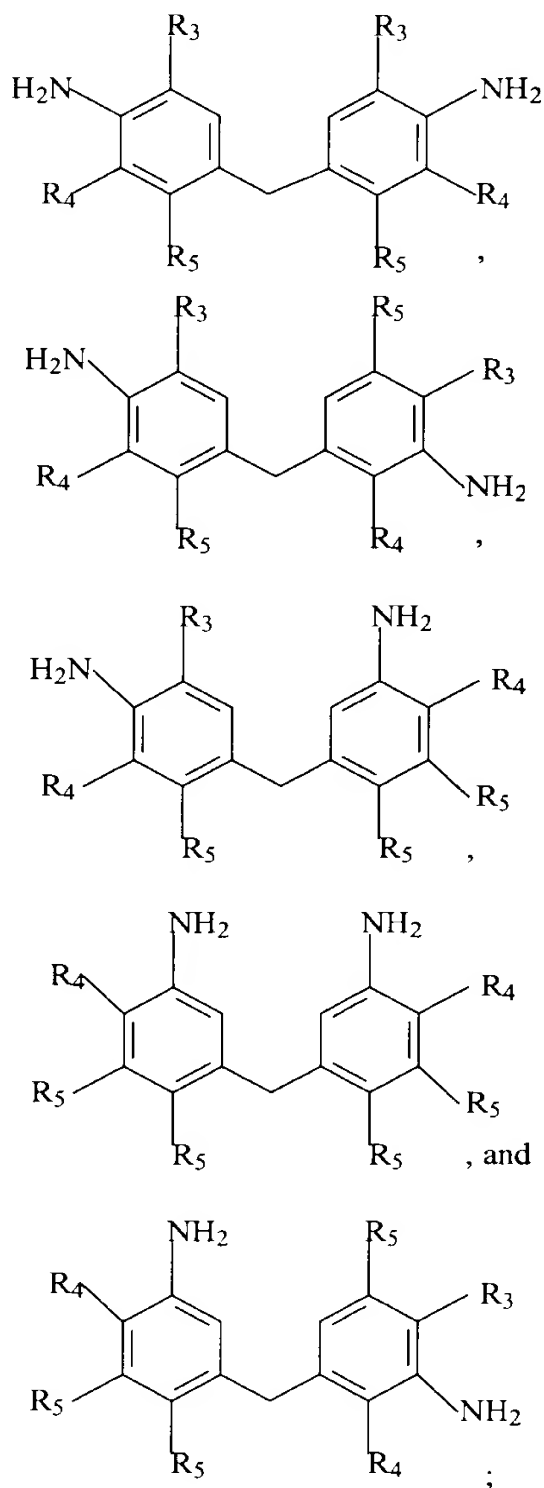
15 a diamine represented by the general formula (B):



and a diamine represented by the general formula (C):

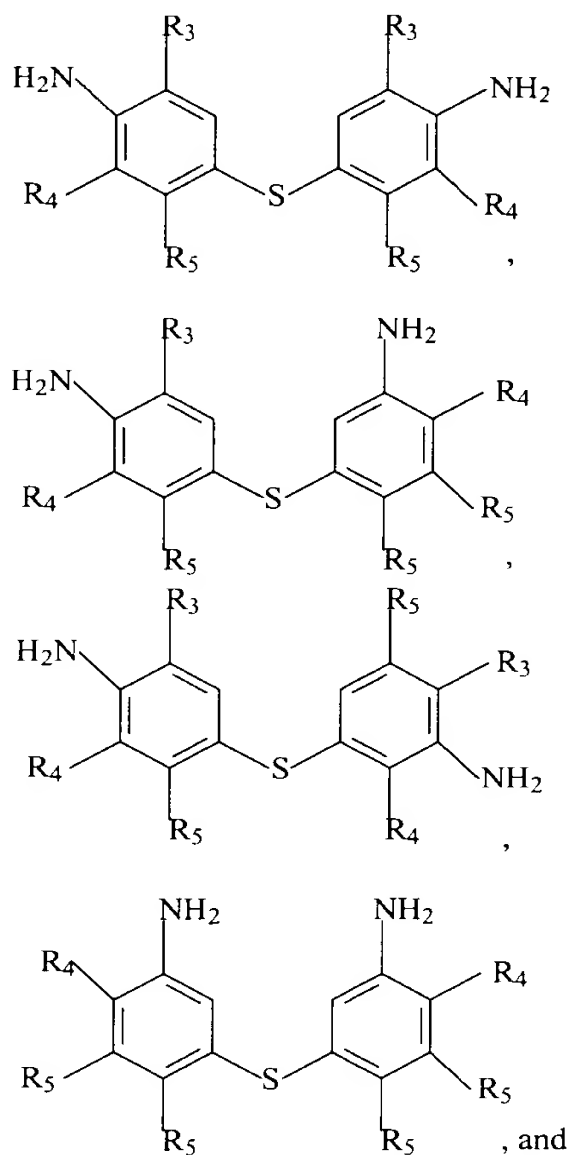


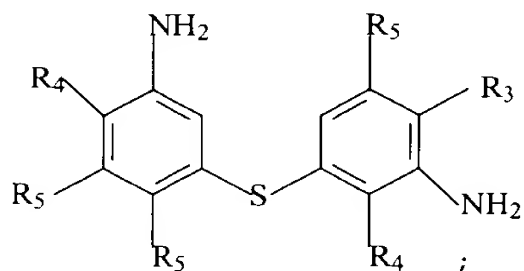
72. The method of claim 71 wherein the diamine of general formula (A) is selected from one or more of the group consisting of:



wherein R_3 and R_4 are each independently C_1 - C_3 alkyl, and R_5 is selected from hydrogen and halogen, and mixtures of said diamines.

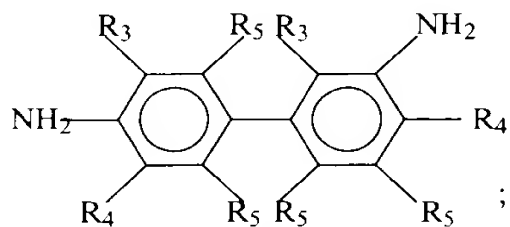
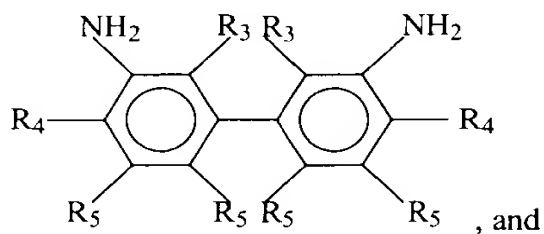
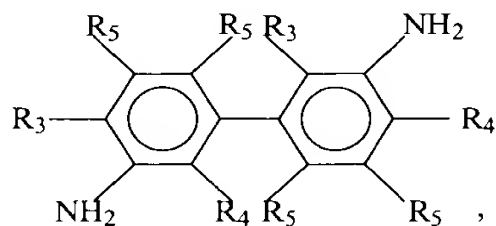
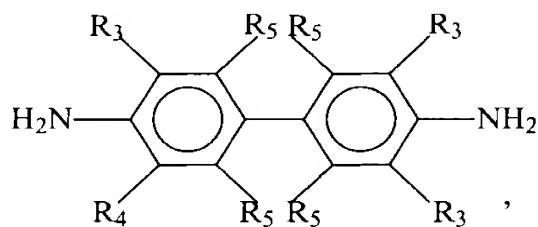
73. The method of claim 71 wherein the diamine of general formula (B) is
5 selected from one or more of the group consisting of:





wherein R_3 and R_4 are each independently C_1 - C_3 alkyl, and R_5 is selected from hydrogen and halogen, and mixtures of said diamines.

74. The method of claim 71 wherein the diamine of general formula (C) is
5 selected from one or more of the group consisting of:



wherein R_3 and R_4 are each independently C_1 - C_3 alkyl, and R_5 is selected from hydrogen and halogen, and mixtures of said diamines.

5 75. The photochromic article of claim 59 wherein a catalyst is added to said two-component composition to promote the polymerization.

76. The photochromic article of claim 75 wherein said catalyst is selected from the group consisting of tertiary amines and organometallic compounds.

10

77. The photochromic article of claim 59 wherein the polymerization process further comprises the step of :

mixing said first component and said second component.

15 78. The photochromic article of claim 59 wherein the polymerization process further comprises the step of :

degassing the said first component.

79. The photochromic article of claim 59 wherein the polymerization process
20 further comprises the step of :

degassing the said second component.

80. The photochromic article of claim 59 wherein the polymerization process further comprises the step of :

25 adding a mixture of said first component and said second component to a mold.

81. The photochromic article of claim 80 wherein the polymerization process further comprises the step of :

30 heating the mold and said mixture within it.

82. The photochromic article of claim 81 wherein said heating step further includes heating the mold and said mixture to a temperature of up to 200°C over a period of from 0.5 to 72 hours.

5 83. The photochromic article of claim 59 wherein said first component and said second component are polymerized together in amounts sufficient to provide a molar equivalent ratio of (NCO + NCS) groups to (-NH₂ + -NH-) groups of from 0.5 to 3.0.

10 84. The photochromic article of claim 59 further comprising additives selected from the group consisting of light stabilizers, heat stabilizers, antioxidants, ultraviolet light absorbers, mold release agents, static (non-photochromic) dyes, pigments and flexibilizing additives and anti-yellowing additives; and mixtures of said additives.

15 85. The photochromic article of claim 84 wherein the additives are present in said polymerizate in an amount up to 10% by weight of said polymerizate.

20 86. The photochromic article of claim 59 further comprising a photochromic substance.

87. The photochromic article of claim 86 wherein the photochromic substance is mixed with said first component.

25 88. The photochromic article of claim 86 wherein the photochromic substance is mixed with said second component.

89. The photochromic article of claim 86 wherein the photochromic substance is applied to said photochromic article at from 0.15 to 0.35 milligrams per square
30 centimeter of surface area of said photochromic article.

90. The photochromic article of claim 86 wherein said photochromic substance is selected from the group consisting of spiro(indoline)naphthoxazines, spiro(indoline)benzoxazines, chromenes, benzopyrans, naphthopyrans, organo-metal dithizonates, (arylaazo)-thioformic arylhydrazidates, mercury dithizonates, fulgides, fulgimides, 3-furyl fulgides, 3-thienyl fulgides, 3-furyl fulgimides and 3-thienyl fulgimide; and mixtures of said photochromic substances.

91. The photochromic article of claim 86 wherein the photochromic substance has an activated absorption maximum within the visible range of from 590 to 700 nanometers.

92. The photochromic article of claim 86 wherein the photochromic substance has an activated absorption maximum within the visible range of from 400 to 500 nanometers.

93. The photochromic article of claim 86 wherein the photochromic substance has an activated absorption maximum within the visible range of from 500 to 700 nanometers.

94. The photochromic article of claim 86 wherein the photochromic substance is applied or incorporated into said photochromic article using a method selected from the list consisting of cast curing, encapsulating within a matrix of an organic polymerizate and incorporating into the two-component composition prior to curing.

95. The photochromic article of claim 86 wherein the photochromic substance is applied by imbibing the photochromic article such that permeation of the photochromic substance into the polymerizate is achieved.

96. The photochromic article of claim 95 wherein the imbibing process includes solvent assisted transfer absorption.

97. The photochromic article of claim 95 wherein the imbibing process includes vapor phase transfer.

98. The photochromic article of claim 95 wherein the photochromic substance
5 is applied as a coating to the surface of the photochromic article.

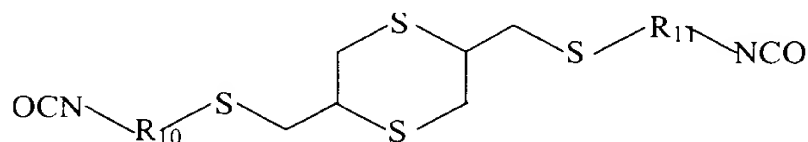
99. The photochromic article of claim 95 wherein the imbibing process includes the steps of:

10 coating the photochromic article with the photochromic substance;
heating the surface of the photochromic article; and
removing the residual coating from the surface of the photochromic article.

100. The photochromic article of claim 86 wherein the photochromic article is an optical lens for correcting a visual defect.

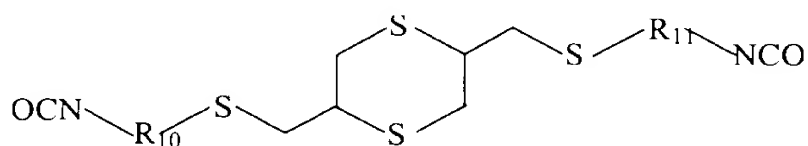
101. The photochromic article of claim 59 wherein said polycyanate monomer has contains one or more sulfur atoms in its backbone.

102. The photochromic article of claim 101 wherein the polycyanate
20 monomer containing one or more sulfur atoms in its backbone has the general structure:



wherein R_{10} and R_{11} are each independently C_1 to C_3 alkyl.

103. The polymerizate of claim 31 wherein the polycyanate monomer
25 containing one or more sulfur atoms in its backbone has the general structure:



wherein R_{10} and R_{11} are each independently C_1 to C_3 alkyl.